Supplementary Material (ESI) for Chemical Communications

Supplementary Information

(1) 1,2,4-TMB isomerization

The catalyst samples were pressed, crushed and sieved to get particles of 14-20 mesh size. The catalytic reaction was carried out in a laboratory-built, up-flow stainless steel reactor (10 mm inside diameter). Samples were analyzed with an online gas chromatograph (equipped with a flame ionization detector, and a fused silica capillary column). In a typical experiment, 100 mg of the sieved catalyst was diluted with 10 parts of 20-mesh sea sand. Prior to the reaction the catalyst was activated for 4 h at 550 °C in air flow. 1,2,4-TMB was fed into the reactor using syringe pump as carried by high purity N_2 flow (WHSV = 4.4 h^{-1}, 20 cc/min N_2 flow rate). The reaction was performed at 400 °C under atmospheric pressure. 1,2,4-TMB conversion and selectivity for various products obtained over three catalysts are given (Table 1).

Table 1 Isomerization reaction of 1,2,4-TMB over various catalysts

Catalysts	**1,2,4-TMB conversion (%)**	**Selectivity (%)**				
		Benzene	**Toluene**	**Xylenes**	**Trimethylbenzene**	**Tetramethylbenzene**
Hierarchical MFI	25.0	0.4	0.5	2.6	91.3	5.2
MFI	30.0	0.9	4.0	21.4	70.8	2.9
Al-MCM-41	11.6	0.2	0.3	4.8	76.9	17.8

(2) Cumene cracking

The catalyst samples were pressed, crushed and sieved to get particles of 14-20 mesh size. The catalytic reaction was carried out in a laboratory-built, up-flow stainless steel reactor (10 mm inside diameter). Samples were analyzed with an online gas chromatograph (equipped with a flame ionization detector, and a fused silica capillary column). In a typical experiment, 100 mg of the sieved catalyst was diluted with 10 parts of 20-mesh sea sand. Prior to the reaction the catalyst was activated for 4 h at 550 °C in air flow. Cumene was fed into the reactor using syringe pump as carried by high purity N_2 flow (WHSV = 7.8 h^{-1}, 60 cc/min N_2 flow rate). The reaction was performed at 350 °C under atmospheric pressure. Cumene conversion and selectivity for various products over three catalysts are given (Table 2).

Table 2 Cumene cracking over various catalysts

Catalysts	**Cumene Conversion (%)**	**Selectivity (%)**					
		Propylene	**C_4-C_6 hydrocarbon**	**Benzene**	**Toluene**	**Ethylbenzene**	**Dipropylbenzene**
Hierarchical MFI	94.3	37.8	3.6	48.2	0.7	0.55	9.1
MFI	97.0	39.3	3.3	49.0	1.6	2.1	4.7
Al-MCM-41	13.6	47.3	1.0	51.7	-	-	-

3. Liquid phase esterification reaction

Liquid phase esterification reaction was carried out under nitrogen atmosphere, using a batch reactor (EYELA Chemi station) equipped with reflux condenser. In a typical esterification reaction, benzyl alcohol (5 mmol), hexanoic acid (5 mmol), toluene (2.5 mL) and catalyst (100 mg) were mixed and the reaction was conducted at 110 °C for 4 h. Samples were analyzed by gas chromatography (Hewlett-Packard 5890 Series II, gas chromatograph equipped with a flame ionization detector and a packed column with 10% SE-30). The products were identified by GC-MS and authentic samples. Quantitative determinations were based on the measured response factors of the reactant and reaction products. After the reaction, reaction mixture was centrifuged to remove the organics. Catalysts were reused as such without any further treatment in recycling experiments. Benzyl alcohol conversion and selectivity for ester and ether over three catalysts in first cycle are given (Table 3).

Table 3 Esterification reaction of benzyl alcohol with hexanoic acid over various catalysts

Catalysts	**Benzyl alcohol conversion (%)**	**Selectivity (%)**	
		Ester	**Ether**
Hierarchical MFI	91.7	75.2	24.8
MFI	23.4	98.2	1.8
Al-MCM-41	82.5	67.0	33.0

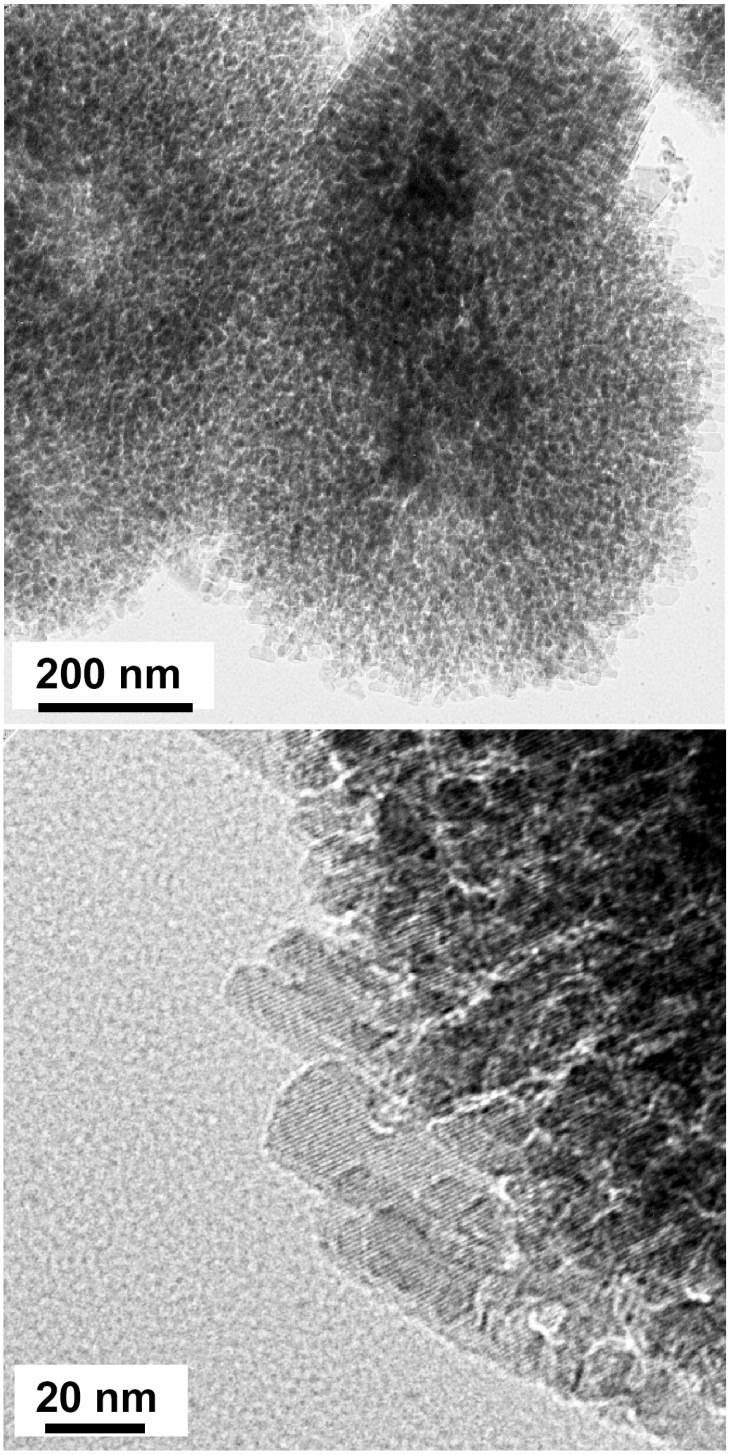

Fig. S1. TEM images of hierarchical MFI zeolite.

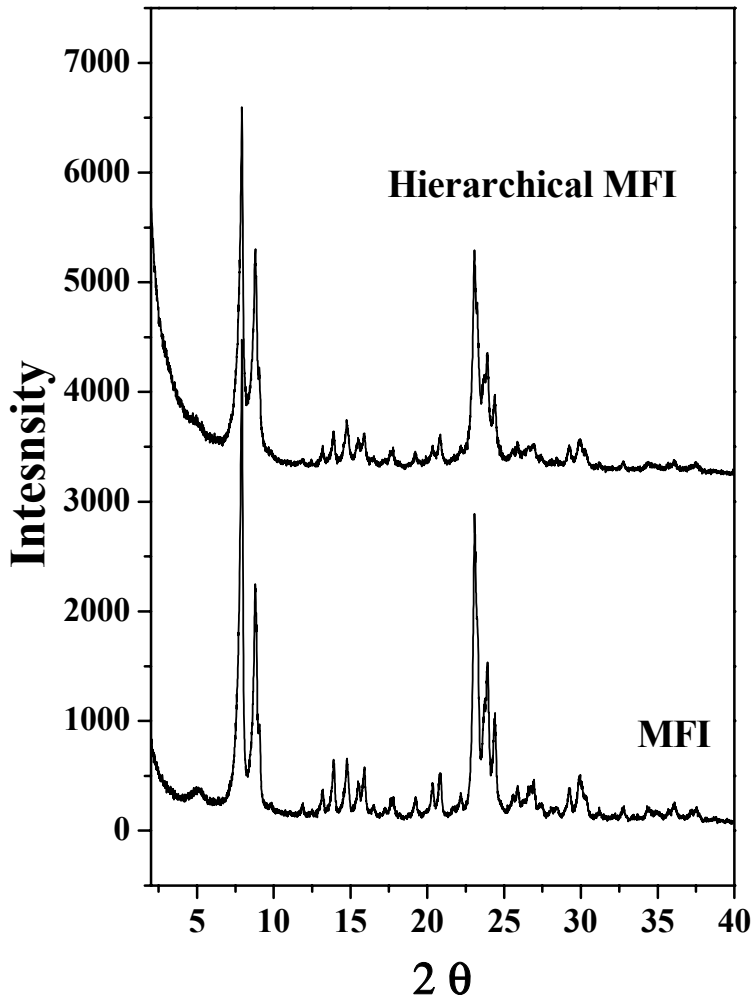

Fig. S2. XRD profiles of hierarchical MFI and conventional MFI.